A MODIFIED GAMBLER'S RUIN MODEL OF POLYETHYLENE CHAINS IN THE AMORPHOUS REGION

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ABSTRACT. Polyethylene chains in the amorphous region between two crystalline lamellae M unit apart are modeled as random walks with one step memory on a cubic lattice between two absorbing boundaries. These walks avoid the two preceding steps, though they are not true self-avoiding walks. Systems of difference equations are introduced to calculate the statistics of the restricted random walks. They yield that the fraction of loops is $(2M-2)/(2M+1)$, the fraction of ties $3/(2M+1)$, the average length of loops $2M-0.5$, the average length of ties $2/3M^2+2/3M-4/3$, the average length of walks equals $3M-3$, the variance of the loop length $16/15M^3+O(M^2)$, the variance of the tie length $28/45M^4+O(M^3)$ and the variance of the walk length $2M^3+O(M^2)$.

INTRODUCTION

Semicrystalline polyethylene formed from melt generally consists of alternating amorphous and crystalline regions. The lengths of the polyethylene chains are many times greater than the lamellar crystal thickness. Each molecule may traverse the amorphous regions and pass through one or more lamellae many times (see ref. 1). A chain which re-enter the same crystal from which it emerges is referred to as a *loop*. A chain which connects the two adjacent crystal lamellae is referred to as a *tie*. The *length* of a walk is the number of steps in the walk, not counting the initial step.

Random walks on a cubic lattice between two parallel absorbing boundaries were employed by Guttman, DiMarzio, and Hoffman to model the polyethylene chains in the amorphous region (see ref. 2). Using the theory of Gambler's ruin statistics (see ref. 3), Guttman *et al.* were able to calculate the statistics of the polyethylene chains. Their results indicate that the fraction of loops is $(M-1)/M$, the fraction of ties $1/M$, the average length of loops $2M$, the average length of ties M^2 and the average length of walks (either loops or ties) equals $3M-2$, where M stands for the thickness of the amorphous region in statistical steps. The Guttman-DiMarzio-Hoffman model, also called the gambler's ruin model, offered an analytic method to calculate the statistics, but it is not entirely satisfactory as a model of polyethylene. Two limitations are: a) Adjacent carbon-carbon bonds in the polyethylene chain are approximately at the tetrahedral angle and at ordinary temperatures this cannot change much. Deviations of the chain from a planar zig-zag (the arrangement actually present inside the crystalline regions) can occur because of *rotations* about carbon-carbon bonds, though these are also somewhat restricted. It has been argued that because of these rotations the direction of the chain at one point can be nearly arbitrary relative to that at a point 3 or 4 bonds away, so that perhaps a walk with random changes of direction at each step could be used as a model, if the step size were taken to correspond to a few C-C bonds (3.5 is commonly used). This is then further simplified to a walk on a cubic lattice, with steps of equal probability in each of the six directions. But the physical significance of the cubic lattice is admittedly rather vague. b) Since the random walks are being used as models for an actual polymer chain, it would be more satisfactory if they were restricted to be "self-avoiding". Because of rather serious technical difficulties associated with self-avoiding walks, however, this has not been done.

In the present paper a modified gambler's ruin model is presented. The cubic lattice idea is retained, but the walks are restricted so as to avoid the two preceding steps. This is by no means a true self-avoiding walk, but goes somewhat in that direction. The results, though similar to those of the original gambler's ruin model, have some significant differences, and so may indicate something of the role of the self-avoidance in this kind of model.

THE MODIFIED GAMBLER'S RUIN MODEL

We consider a random walk on a cubic lattice between two parallel absorbing planes at $z=0$ and $z=M$ respectively. The walk starts at a lattice point on the $z=0$ plane and goes up in the first step. It is continued on the lattice with a probability $1/5$ of preceding to any one of the adjacent lattice points except the one that it just visited. The walk terminates when it reaches the $z = 0$ plane (where a loop is formed) or the $z = M$ plane (where a tie is formed).

Fractions of Loops and Ties. Let s_1, s_0, s_{-1} be a step going up, horizontally and down in the z direction respectively. Let $P_k(a|s_i)$ be the probability that a walk will be absorbed at $z = a$ ($a = 0$ or M) given that it starts at a point on $z = k$ $(0 < k < M)$ with a preceding step s_i. After the first step the position of the walk is at $z = k+1$, k or $k-1$. Since no reverse step is allowed, we must have

$$\left.\begin{aligned} P_k(a|s_1) &= \frac{1}{5}P_{k+1}(a|s_1) + \frac{4}{5}P_k(a|s_0), \\ P_k(a|s_0) &= \frac{1}{5}P_{k+1}(a|s_1) + \frac{3}{5}P_k(a|s_0) + \frac{1}{5}P_{k-1}(a|s_{-1}), \\ P_k(a|s_{-1}) &= \frac{4}{5}P_k(a|s_0) + \frac{1}{5}P_{k-1}(a|s_{-1}), \end{aligned}\right\} \qquad [\mathbf{1}]$$

for $0 < k < M$. Since the walk terminates when it for the first time reaches either 0 or M, we define

$$P_0(0|s_{-1}) = 1, \qquad P_0(M|s_{-1}) = 0, \qquad P_M(0|s_1) = 0, \qquad P_M(M|s_1) = 1. \qquad [\mathbf{2}]$$

We now let E be the shift operator defined by $E^n k = k + n$. Eqs. **1** can be written in a matrix form as

$$\begin{pmatrix} 1 - \frac{1}{5}E & -\frac{4}{5} & 0 \\ -\frac{1}{5}E & \frac{2}{5} & -\frac{1}{5}E^{-1} \\ 0 & -\frac{4}{5} & 1 - \frac{1}{5}E^{-1} \end{pmatrix} \begin{pmatrix} P_k(a|s_1) \\ P_k(a|s_0) \\ P_k(a|s_{-1}) \end{pmatrix} = \mathbf{0}. \qquad [\mathbf{3}]$$

The probability for a walk to be a loop is $P_1(0|s_1)$ and to be a tie $P_1(M|s_1)$.

The Expected Length of a Loop or a Tie. Let $P_k(D|s_i, a)$ be the probability that a walk has length D given that the walk starts at $z = k$ with a preceding step s_i and terminates at $z = a$ ($a = 0$ or M). The expected length of such a walk is $\sum_{D=0}^{\infty} D \cdot P_k(D|s_i, a)$. We now let $P_k(a, D|s_i)$ be the probability that a walk terminates at $z = a$ and has length D given that the walk starts at $z = k$ with a preceding step s_i. After the first step the walk is at either $k+1$, k or $k-1$. We conclude that for $0 < k < M$ and $D > 0$,

$$\left.\begin{aligned}
P_k(a,D|s_1) &= \frac{1}{5}P_{k+1}(a,D-1|s_1)+\frac{4}{5}P_k(a,D-1|s_0),\\
P_k(a,D|s_0) &= \frac{1}{5}P_{k+1}(a,D-1|s_1)+\frac{3}{5}P_k(a,D-1|s_0)+\frac{1}{5}P_{k-1}(a,D-1|s_{-1}),\\
P_k(a,D|s_{-1}) &= \frac{4}{5}P_k(a,D-1|s_0)+\frac{1}{5}P_{k-1}(a,D-1|s_{-1}).
\end{aligned}\right\} \qquad [\mathbf{4}]$$

Now let $L_k(a|s_i)=\sum_{D=0}^{\infty} D\cdot P_k(a,D|s_i)$. By using Eqs. **4** we have, for $0<k<M$,

$$\begin{aligned}
L_k(a|s_1) = \sum_{D=0}^{\infty} D\cdot P_k(a,D|s_1) &= \sum_{D=1}^{\infty} D\cdot P_k(a,D|s_1)\\
&=\frac{1}{5}\sum_{D=1}^{\infty} D\cdot P_{k+1}(a,D-1|s_1)+\frac{4}{5}\sum_{D=1}^{\infty} D\cdot P_k(a,D-1|s_0)\\
&=\frac{1}{5}\sum_{D=0}^{\infty}(D+1)P_{k+1}(a,D|s_1)+\frac{4}{5}\sum_{D=0}^{\infty}(D+1)P_k(a,D|s_0)\\
&=\frac{1}{5}\sum_{D=0}^{\infty} D\cdot P_{k+1}(a,D|s_1)+\frac{4}{5}\sum_{D=0}^{\infty} D\cdot P_k(a,D|s_0)\\
&\quad+\frac{1}{5}\sum_{D=0}^{\infty} P_{k+1}(a,D|s_1)+\frac{4}{5}\sum_{D=0}^{\infty} P_k(a,D|s_0)\\
&=\frac{1}{5}L_{k+1}(a|s_1)+\frac{4}{5}L_k(a|s_0)+\frac{1}{5}P_{k+1}(a|s_1)+\frac{4}{5}P_k(a|s_0)\\
&=\frac{1}{5}L_{k+1}(a|s_1)+\frac{4}{5}L_k(a|s_0)+P_k(a|s_1).
\end{aligned} \qquad [\mathbf{5}]$$

Similarly, it is easy to show

$$\left.\begin{aligned}
L_k(a|s_0) &= \frac{1}{5}L_{k+1}(a|s_1)+\frac{3}{5}L_k(a|s_0)+\frac{1}{5}L_{k-1}(a|s_{-1})+P_k(a|s_0),\\
L_k(a|s_{-1}) &= \frac{4}{5}L_k(a|s_0)+\frac{1}{5}L_{k-1}(a|s_{-1})+P_k(a|s_{-1}).
\end{aligned}\right\} \qquad [\mathbf{6}]$$

Since $P_0(a,D|s_i)=P_M(a,D|s_i)=0$ for all $D>0$, we have the boundary conditions

$$L_0(a|s_{-1})=0, \qquad L_M(a|s_1)=0. \qquad [\mathbf{7}]$$

Write Eqs. **5** and **6** in a matrix form,

$$\begin{pmatrix} 1-\frac{1}{5}E & -\frac{4}{5} & 0 \\ -\frac{1}{5}E & \frac{2}{5} & -\frac{1}{5}E^{-1} \\ 0 & -\frac{4}{5} & 1-\frac{1}{5}E^{-1} \end{pmatrix} \begin{pmatrix} L_k(a|s_1) \\ L_k(a|s_0) \\ L_k(a|s_{-1}) \end{pmatrix} = \begin{pmatrix} P_k(a|s_1) \\ P_k(a|s_0) \\ P_k(a|s_{-1}) \end{pmatrix}. \qquad [\mathbf{8}]$$

It follows from the property of the conditional probability $P(A|BC) = \dfrac{P(AB|C)}{P(B|C)}$ (*i.e.*, the conditional probability of A for given B and C is equal to the conditional probability of the occurrence of both A and B for given C divided by the conditional probability of B on the hypothesis C) that

$$P_k(D|s_i, a) = \frac{P_k(a, D|s_i)}{P_k(a|s_i)}.$$

Therefore, the expected length of a loop $= \sum_{D=0}^{\infty} D \cdot P_1(D|s_1, 0) = \dfrac{L_1(0|s_1)}{P_1(0|s_1)}$ and of a tie $= \sum_{D=0}^{\infty} D \cdot P_1(D|s_1, M) = \dfrac{L_1(M|s_1)}{P_1(M|s_1)}$ (not counting the first step).

The rth Order Moments of the Loop Length and the Tie Length. Similarly, the rth order moment of the expected length can be calculated. Let $r \geq 1$ be an integer. The rth moment of the loop length or the tie length is $\sum_{D=0}^{\infty} D^r \cdot P_k(D|s_i, 0)$ and $\sum_{D=0}^{\infty} D^r \cdot P_k(D|s_i, M)$, respectively. Let $M_k^r(a|s_i) = \sum_{D=0}^{\infty} D^r \cdot P_k(a, D|s_i)$. Using Eqs. **4**, it is easy to show that for $0 < k < M$

$$\begin{pmatrix} 1-\frac{1}{5}E & -\frac{4}{5} & 0 \\ -\frac{1}{5}E & \frac{2}{5} & -\frac{1}{5}E^{-1} \\ 0 & -\frac{4}{5} & 1-\frac{1}{5}E^{-1} \end{pmatrix} \begin{pmatrix} M_k^r(a|s_1) \\ M_k^r(a|s_0) \\ M_k^r(a|s_{-1}) \end{pmatrix}$$

$$= \begin{pmatrix} P_k(a|s_1) \\ P_k(a|s_0) \\ P_k(a|s_{-1}) \end{pmatrix} + \sum_{i=1}^{r-1} \frac{r!}{i!(r-i)!} \begin{pmatrix} M_k^i(a|s_1) \\ M_k^i(a|s_0) \\ M_k^i(a|s_{-1}) \end{pmatrix} \qquad [\mathbf{9}]$$

and the boundary conditions

$$M_0^r(a|s_{-1}) = 0, \qquad M_M^r(a|s_1) = 0. \qquad [\mathbf{10}]$$

The rth moment of a loop $= \sum_{D=0}^{\infty} D^r \cdot P_1(D|s_1, 0) = \dfrac{M_1^r(0|s_1)}{P_1(0|s_1)}$ and of a tie $= \sum_{D=0}^{\infty} D^r \cdot P_1(D|s_1, M) = \dfrac{M_1^r(M|s_1)}{P_1(M|s_1)}$.

THE SOLUTIONS OF THE SYSTEMS OF DIFFERENCE EQUATIONS

The solution of Eqs. 1 and 2. Applying the method of solution by elimination to Eqs. **3** for $a = 0$, we have three independent higher order difference equations:

$$\left.\begin{aligned} &P_{k+1}(0|s_1) - 2P_k(0|s_1) + P_{k-1}(0|s_1) = 0, \\ &P_{k+1}(0|s_0) - 2P_k(0|s_0) + P_{k-1}(0|s_0) = 0, \\ &P_{k+1}(0|s_{-1}) - 2P_k(0|s_{-1}) + P_{k-1}(0|s_{-1}) = 0, \end{aligned}\right\} \qquad [\mathbf{11}]$$

Hence, all the solutions $P_k(0|s_1)$, $P_k(0|s_0)$ and $P_k(0|s_{-1})$ have the form $c_0 + c_1 k$. We now let

$$P_k(0|s_1) = \alpha_0 + \alpha_1 k, \qquad P_k(0|s_0) = \beta_0 + \beta_1 k, \qquad P_k(0|s_{-1}) = \gamma_0 + \gamma_1 k. \qquad [\mathbf{12}]$$

Since $P_k(0|s_1) = P_{M-k}(M|s_{-1}) = 1 - P_{M-k}(0|s_{-1})$, we must have $\gamma_1 = \alpha_1$ and $\gamma_0 = 1 - \alpha_0 - \alpha_1 M$. Substituting Eqs. **12** into Eqs. **3** and equating the coefficients of like functions on both sides gives

$$\left.\begin{aligned} &\alpha_1 - \beta_1 = 0, \\ &4\alpha_0 - \alpha_1 - 4\beta_0 = 0, \\ &M\alpha_1 + 2\beta_0 = 1, \\ &4\alpha_0 + (4M-1)\alpha_1 + 4\beta_0 = 4, \end{aligned}\right\} \qquad [\mathbf{13}]$$

(of which only 3 are independent). To solve Eqs. **11** and satisfy the boundary conditions (Eqs. **2**), we must choose α_0, α_1, β_0 and β_1 to satisfy Eqs. **13** and

$$\alpha_0 + \alpha_1 M = 0. \qquad [\mathbf{14}]$$

That is,

$$\begin{aligned} \alpha_0 &= \frac{2M}{2M+1}, \qquad & \alpha_1 &= -\frac{2}{2M+1}, \\ \beta_0 &= \frac{4M+1}{2(2M+1)}, \qquad & \beta_1 &= -\frac{2}{2M+1}. \end{aligned}$$

Therefore, we have, for $0 < k < M$

$$\left.\begin{aligned} P_k(0|s_1) &= \frac{2M}{2M+1} - \frac{2}{2M+1}k, \\ P_k(0|s_0) &= \frac{4M+1}{2(2M+1)} - \frac{2}{2M+1}k, \\ P_k(0|s_{-1}) &= 1 - \frac{2}{2M+1}k. \end{aligned}\right\} \qquad [\mathbf{15}]$$

Since $P_k(M|s_i) = 1 - P_k(0|s_i)$, it is clear that

$$\left.\begin{aligned} P_k(M|s_1) &= \frac{1}{2M+1} + \frac{2}{2M+1}k, \\ P_k(M|s_0) &= \frac{1}{2(2M+1)} + \frac{2}{2M+1}k, \\ P_k(M|s_{-1}) &= \frac{2}{2M+1}k. \end{aligned}\right\} \qquad [\mathbf{16}]$$

The solution of Eqs. 7 and 8. Use the above results and apply the same method to Eqs. **8**:

$$\left.\begin{aligned} L_{k+1}(0|s_1) - 2L_k(0|s_1) + L_{k-1}(0|s_1) &= \frac{8(k-M)}{2M+1}, \\ L_{k+1}(0|s_0) - 2L_k(0|s_0) + L_{k-1}(0|s_0) &= \frac{8(k-M)-2}{2M+1}, \\ L_{k+1}(0|s_{-1}) - 2L_k(0|s_{-1}) + L_{k-1}(0|s_{-1}) &= \frac{8(k-M)-4}{2M+1}, \end{aligned}\right\} \qquad [\mathbf{17}]$$

and

$$\left.\begin{aligned} L_{k+1}(M|s_1) - 2L_k(M|s_1) + L_{k-1}(M|s_1) &= \frac{-8k-4}{2M+1}, \\ L_{k+1}(M|s_0) - 2L_k(M|s_0) + L_{k-1}(M|s_0) &= \frac{-8k-2}{2M+1}, \\ L_{k+1}(M|s_{-1}) - 2L_k(M|s_{-1}) + L_{k-1}(M|s_{-1}) &= \frac{-8k}{2M+1}. \end{aligned}\right\} \qquad [\mathbf{18}]$$

for $0 < k < M$.

Solving the above nonhomogeneous difference equations under the boundary conditions (Eqs. **7**), we have

$$\left.\begin{aligned}
L_k(0|s_1) &= \frac{4}{3(2M+1)}k^3 - \frac{4M}{2M+1}k^2 + \frac{8M^2-4M-1}{3(2M+1)}k + \frac{M(4M+1)}{3(2M+1)},\\
L_k(0|s_0) &= \frac{4}{3(2M+1)}k^3 - \frac{4M+1}{2M+1}k^2 + \frac{16M^2+4M+7}{6(2M+1)}k + \frac{8M^2-10M-3}{12(2M+1)},\\
L_k(0|s_{-1}) &= \frac{4}{3(2M+1)}k^3 - 2k^2 + \frac{2}{3}(2M+1)k,
\end{aligned}\right\} \qquad [\mathbf{19}]$$

and

$$\left.\begin{aligned}
L_k(M|s_1) &= -\frac{4}{3(2M+1)}k^3 - \frac{2}{2M+1}k^2 + \frac{4M^2+4M-2}{3(2M+1)}k + \frac{2M(M+1)}{3(2M+1)},\\
L_k(M|s_0) &= -\frac{4}{3(2M+1)}k^3 - \frac{1}{2M+1}k^2 + \frac{8M^2+8M-7}{6(2M+1)}k + \frac{4M^2+4M-3}{12(2M+1)},\\
L_k(M|s_{-1}) &= -\frac{4}{3(2M+1)}k^3 + \frac{1}{3}(2M+1)k.
\end{aligned}\right\} \qquad [\mathbf{20}]$$

The solution of Eqs. 9 and 10. Similarly, solving Eqs. **9** and **10** for $r = 2$ gives

$$\left.\begin{aligned}
&M_k^2(0|s_1)\\
&\quad= -\frac{8}{15(2M+1)}k^5 + \frac{8M}{3(2M+1)}k^4 - \frac{2(16M^2-8M-9)}{9(2M+1)}k^3 - \frac{2M(8M+9)}{3(2M+1)}k^2\\
&\qquad+ \frac{4(32M^5+80M^4+90M^3-20M^2-35M+6)}{45(2M+1)^2}k\\
&\qquad+ \frac{4(M+1)M(16M^3+24M^2+41M-6)}{45(2M+1)^2},\\
&M_k^2(M|s_1)\\
&\quad= \frac{8}{15(2M+1)}k^5 + \frac{4}{3(2M+1)}k^4 - \frac{2(8M^2+8M+3)}{9(2M+1)}k^3 - \frac{8M^2+8M+7}{3(2M+1)}k^2\\
&\qquad+ \frac{2(56M^5+140M^4+150M^3+85M^2-20M-42)}{45(2M+1)^2}k\\
&\qquad+ \frac{M(56M^4+140M^3+190M^2+145M+84)}{45(2M+1)^2},
\end{aligned}\right\} \qquad [\mathbf{21}]$$

and the expressions for $M_k^2(0|s_0)$, $M_k^2(0|s_{-1})$, $M_k^2(M|s_0)$ and $M_k^2(M|s_{-1})$, which can be further used to solve higher order moments of the expected lengths of walks.

THE STATISTICS OF THE RESTRICTED RANDOM WALKS

Letting $k = 1$ in Eqs. **15**, **16**, **19**, **20** and **21**, we get

$P_1(0|s_1) = 1 - \dfrac{3}{2M+1}, \qquad P_1(M|s_1) = \dfrac{3}{2M+1},$

$L_1(0|s_1) = \dfrac{4M^2 - 5M + 1}{2M+1}, \qquad L_1(M|s_1) = \dfrac{2(M^2 + M - 2)}{2M+1},$

$M_1^2(0|s_1) = \dfrac{2(M-1)(32M^4 + 112M^3 + 82M^2 + 2M - 15)}{15(2M+1)^2,}$

and $M_1^2(M|s_1) = \dfrac{(M-1)(M+1)(56M^3 + 140M^2 + 86M + 45)}{15(2M+1)^2}.$

Hence,

the probability for a walk to be a loop $P_0 = 1 - \dfrac{3}{2M+1}$,

the probability for a walk to be a tie $P_M = \dfrac{3}{2M+1}$,

the expected length of a loop $L_0 = 2M - \dfrac{1}{2}$,

the expected length of a tie $L_M = \dfrac{2}{3}M^2 + \dfrac{2}{3}M - \dfrac{4}{3}$,

the expected length of a walk $= P_0 L_0 + P_M L_M = 3M - 3$,

the variance of the loop length $\sigma_0^2 = \dfrac{32M^4 + 112M^3 + 82M^2 + 2M - 15}{15(2M+1)}$,

the variance of the tie length $\sigma_M^2 = \dfrac{(M-1)(M+1)(56M^3 + 140M^2 + 86M + 45)}{45(2M+1)}$,

the variance of the walk length $\sigma = P_0\sigma_0^2 + P_M\sigma_M^2 = (M-1)(2M^2 + 5M + 1)$.

DISCUSSION

Mechanical properties of semicrystalline polymeric materials depend on the entanglement and configurations of molecular chains which comprise them (see ref. 1). People believe that the entanglements are provided by the chain loops and ties. This model calculated the statistics of loops and ties. The expected length of a walk and the expected length of a loop are statistically the same as those yielded by the gambler's ruin model, but the predicted probabilities of a walk to be a loop or a tie and the expected length of a tie are different between these two models.

The self-avoiding random walk problem has received much attention. There are a number of sophisticated approximate analytical theories (see ref. 4.), but no complete analytical solution has been forthcoming. In principle, the random walk in this model can be extended to memorize any finite number of preceding steps, but the process to find and solve the corresponding systems of difference equations could be very complex. An elegant method is yet to be found to completely solve the self-avoidance problem analytically.

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